APPLICATION OF THE ELEMENT POTENTIAL METHOD TO GASEOUS CHEMICAL EQUILIBRIUM CALCULATION

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Joseph Richard Wrobel

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ABSTRACT

The equilibrium state of a mixture of chemically reacting perfect gases at fixed enthalpy and pressure is formulated in terms of the Massieu element potentials by the application of the entropy maximization principle. An iterative solution technique is presented to obtain the parameters appropriate to the equilibrium state. A method for obtaining starting values and a stability criterion based upon the element potential method are presented. A perturbation technique is developed to predict the equilibrium state for different enthalpy, pressure, and atomic mole number constraints, given the solution for one set of constraints.

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SUMMARY

The equilibrium state of a mixture of chemically reacting perfect gases is described by the application of the maximization of entropy principle for the case of fixed enthalpy, pressure, and atomic specie mole numbers. The conditions at equilibrium are formulated in terms of the Massieu element potentials and the temperature; there being one element potential for each distinct atomic type in the mixture.

An iterative method of relaxing the element potentials and the temperature to their respective equilibrium values is presented. The exponential dependence of the partial pressures upon the potentials and the logarithmic form that is selected for the temperature guarantee the non-negativity of pressure and temperature at each step in the iteration. A stability criterion based upon the concavity of the entropy function in the variable space is developed as an aid to obtain rapid convergence. Since the number of atomic types is, in general, less than the number of molecular species considered in the reaction, the rank of the solution matrix is less than that for solution methods not using the element potential technique. The simultaneous relaxation of temperature with composition eliminates the need for subsequent interpolations. A method of estimating accurate starting values for the iteration is developed, and requires only that one guess the approximate temperature.

A perturbation method for predicting the equilibrium state for small changes in the enthalpy, pressure, and atomic mole numbers is evolved from the iterative solution technique. The results of the iterative method presented, as well as those for the perturbation analysis, are compared with digital computer calculations based upon another analytic approach for nitrogen tetroxide and hydrazine combustion. The results compare to within a few percent, the difference being due largely to the numerical inaccuracies incurred in interpolating property data tables.

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Part I

INTRODUCTION

The determination of the state of thermodynamic equilibrium for a chemically reacting gas mixture of fixed total enthalpy is a problem of daily occurrence in the field of chemical rocketry. The problem is readily resolved to that of determining the solution to a set of non-linear algebraic equations by an iterative method. The thermodynamic formulation of the problem determines the character of these equations, and therefore greatly influences the complexity of obtaining a solution. Through the years a considerable number of approaches have been presented, both in the thermodynamic formulation and in the solution technique. The methods of (1)-(3)* are representative of these. The foremost complicating feature of the problem is the demand that the formulation and solution technique be sufficiently general to permit rapid convergence to the equilibrium state from arbitrary initial parameter estimates. The present approach is a simple, yet exact and general, thermodynamic formulation coupled with a solution technique possessing a thermodynamic criterion of solution stability, a minimum number of iterated variables, and a method for determining starting values requiring only the estimation of the thermodynamic temperature. The approach is quite amenable to

*Numbers in parenthesis refer to the bibliography on page 49

either hand calculation or digital computation on small electronic computers.

Part II

DESCRIPTION OF THE EQUILIBRIUM STATE*

To begin, a closed system is defined. The concept of closure is defined with respect to heat transfer, mass transfer, and all types of work. For this analysis the types of work are restricted to hydrostatic mechanical work. The system is composed of an assembly of gaseous, chemically reacting molecules. Such a system may be completely specified by assigning: an extensive parameter to the lumped internal degrees of freedom, the interal energy (U); an extensive parameter to the geometric degrees of freedom, the volume (V); and a set of extensive parameters to the chemical degrees of freedom, the mole numbers (N_i). The subscript i ranges from 1 to C, the number of discreet molecular species in the mixture. The differential parameter dU is a measure of the heat transfer to the internal degrees of freedom of the molecular species. The differential parameter dV is a measure of the hydrostatic work done on or by the system. The differential parameters dN_i are a measure of the mass transfer to or from the system.

For the system described in the preceeding, we may postulate the entropy function (S), which possesses the following properties:

a. S is a continuous and differentiable function of the extensive parameters.

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*Portions of this development have been abstracted from Blatz and Wrobel (4).

b. S is a monotonically increasing function of U.

c. S is a maximum in the equilibrium state.

d. S approaches the limit zero as $\left(\frac{\partial U}{\partial S}\right)_{V, N_i}$ approaches zero.

If we further define the derivatives with respect to the extensive parameter as follows,

$$\left(\frac{\partial S}{\partial U}\right)_{V, N_i} \equiv \frac{1}{T} \tag{1a.}$$

$$\left(\frac{\partial S}{\partial V}\right)_{U, N_i} \equiv \frac{P}{T} \tag{1b.}$$

$$\left(\frac{\partial S}{\partial N_i}\right)_{U, V, N_{j \neq i}} \equiv -\frac{\mu_i}{T} \tag{1c.}$$

we arrive at the differential form of the entropy function

$$dS = \frac{dU}{T} + \frac{P}{T}\, dV - \sum_i \frac{\mu_i}{T}\, dN_i \tag{2}$$

Callen (5) illustrates that these properties of the entropy function are compatible with the conventional statements of the laws of thermodynamics. The resulting postulatory form of the entropy function is, of course, identical with the phenomenalogical formulation of Gibbs (6).

In a chemically reacting system, the concept of closure with respect to mass transfer requires the preservation of atomic species. The conservation of atoms dictates that

$$\{N^\alpha\} = \left\{ \sum_i \omega_i^\alpha N_i \right\} \qquad 1 \leq i \leq C \qquad 1 \leq \alpha \leq A \tag{3}$$

where:

a. ω_i^{α} is the number of atoms of type α in molecular species i

b. the total number of types of atomic species is equal to A

c. N^{α} is the number of gram atoms of type α per unit mass of system.

The N^{α} possess the property that

$$\sum_{\alpha} A^{\alpha} N^{\alpha} = 1 \tag{4}$$

where A^{α} is the atomic weight of atomic species α. The total mass of the system is taken to be unity.

In the light of these definitions, consider the differential form of the entropy function for a process in which the enthalpy and pressure are to remain fixed, i.e.,

$$dH = d(U + PV) = 0 \tag{5a.}$$

$$dP = 0 \tag{5b.}$$

The differential form of the entropy function (equation 2) becomes

$$dS = \frac{d(U+PV)}{T} - \frac{V}{T} dP - \sum_i \frac{\mu_i}{T} dN_i \tag{6}$$

$$= \quad 0 \quad - \quad 0 \quad - \sum_i \frac{\mu_i}{T} dN_i$$

In the equilibrium state S is to be a maximum and therefore for a virtual process dS shall be zero, subject to the mass balance constraints. To determine the solution for this constrained maximization problem, the method of Lagrange

multipliers* is applied. Define the new function ϕ,

$$\phi \equiv S + \sum_{\alpha} \lambda^{\alpha} N^{\alpha} \tag{7}$$

where the λ^{α} are the constant Lagrange multipliers, one for each atomic species constraint. Optimizing the ϕ function with respect to the composition variables evolves equation 8.

$$\frac{\partial \phi}{\partial N_i} = 0 = \frac{\partial S}{\partial N_i} + \sum_{\alpha} \lambda^{\alpha} \frac{\partial N^{\alpha}}{\partial N_i} \qquad 1 \leq i \leq C \tag{8}$$

The entropy derivatives are evaluated from the postulated properties of the entropy function presented in equation 1.

From the mass balance constraints of equation 3, the composition derivatives are obtained, i.e.,

$$\frac{\partial N^{\alpha}}{\partial N_i} = \omega_i^{\alpha} \tag{9}$$

Therefore, for each molecular specie in the mixture at the equilibrium state, the substitution of equations 8 and 9 into equation 6 reveals that

$$\frac{\mu_i}{T} = \sum_{\alpha} \lambda^{\alpha} \omega_i^{\alpha} \tag{10}$$

The same result is obtained for fixed U and V. The chemical Massieu potential ($\mu i/T$) of molecular species i existing in the equilibrium mixture can be decomposed into Massieu element potentials λ^{α}, there being one element potential for each atomic species α. For example, at equilibrium

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*See Sokolnikoff and Redheffer (7) for a description of this method of determining constrained optima

$$\frac{\mu_{H_2O}}{T} = \lambda^O + 2\lambda^H \tag{11a.}$$

$$\frac{\mu_{CO_2}}{T} = \lambda^C + 2\lambda^O \tag{11b.}$$

To determine the maximum value of the entropy, subject to the constraints, equation 10 is multiplied through by N_i and summed over i

$$\sum_i \frac{N_i \mu_i}{T} \equiv \frac{F}{T} = \sum_\alpha \sum_i \lambda^\alpha N_i \omega_i^\alpha = \sum_\alpha N^\alpha \lambda^\alpha \tag{12}$$

However, since

$$\phi = S + \sum_\alpha \lambda^\alpha N^\alpha = S + F/T \tag{13}$$

and

$$\frac{F}{T} = \frac{H}{T} - S \tag{14}$$

the value of the entropy in the equilibrium state is

$$S = \frac{H}{T} - \sum_\alpha \lambda^\alpha N^\alpha \tag{15}$$

The equilibrium state is specified in terms of the A + 1 quantities $\{\lambda^\alpha\}$, T. It is proposed that the solution of the equilibrium problem be performed by relaxing $\{\lambda^\alpha\}$ and T by an iterative technique to their respective equilibrium values. This amounts to the solution of a constrained maximum problem by iteration upon the Lagrange multipliers, which take on the identity of element potentials for this problem. It shall be illustrated that starting values of the parameters are easily estimated and rapidly relaxed to the equilibrium values.

Part III

AN ITERATIVE SOLUTION TECHNIQUE

A relaxation procedure for determining the equilibrium state is now presented for the system under study. The enthalpy of such a perfect gas mixture, at equilibrium, shall be equal to the specified enthalpy H, as in equation 16.

$$H - \sum_i N_i h_i = 0 \tag{16}$$

The mass balance constraints require that

$$\{N^\alpha\} - \left\{\sum_i N_i \omega_i^\alpha\right\} = 0 \tag{17}$$

The equilibrium state is described by the element potentials, as in equation 18.

$$\frac{\mu_i}{T} = \frac{\mu_i^+}{T} + R \ln p_i/p^+ = \sum_\alpha \lambda^\alpha \omega_i^\alpha \tag{18}$$

Here μ_i^+ is the standard free energy of molecular specie i at temperature T, and p^+ is the standard pressure, usually taken to be 1 atmosphere. The remaining relation to be applied is that relating the partial pressures to the mole fractions for perfect gases; the Gibbs-Dalton Law of equation 19.

$$\frac{N_i}{N} = \frac{p_i}{P} \tag{19}$$

where N, the total number of moles, is defined as $N = \sum_i N_i$. Among these equations, the mole numbers may be eliminated at the outset by ratioing, i.e.,

$$\frac{N^\alpha}{H} = \frac{\Sigma N_i \omega_i^\alpha}{\Sigma N_i h_i} = \frac{N \Sigma p_i/p \, \omega_i^\alpha}{N \Sigma p_i/p \, h_i} \tag{20}$$

To abbreviate the notation, it is convenient to define an averaging operation

$$\langle \chi \rangle \equiv \sum_i p_i/P \; \chi_i$$

Equation 20 may then be abbreviated to

$$\frac{N^\alpha}{H} = \frac{\langle \omega^\alpha \rangle}{\langle \mathcal{R} \rangle} \tag{21}$$

For the pressure constraint, equation 22 applies.

$$\sum_i p_i/P = 1 = \langle 1 \rangle \tag{22}$$

The antilog of equation 18 presents the partial pressures explicitly in equation 23.

$$\frac{p_i}{P} = \frac{p^+}{P} \exp\left[\sum_\alpha \frac{\lambda^\alpha \omega_i^\alpha}{\mathcal{R}} - \frac{\mu_i^+}{\mathcal{R}T} \right] \tag{23}$$

For a given estimate of $\{\lambda_n^\alpha\}$ & T_n, where subscript $\underline{n}$ implies the n'th estimate, errors will occur in the enthalpy, mass balance and pressure unless the equilibrium values were estimated precisely. These errors result in an imbalance, or residual, in the various constraint equations. Define the following functions for each iteration

$$\Delta_n^p = \langle 1 \rangle - 1 \tag{24a.}$$

$$\Delta_n^\alpha = \frac{N^\alpha}{H} \frac{\langle \mathcal{R} \rangle}{\langle \omega^\alpha \rangle} - 1 \tag{24b.}$$

In the equilibrium state, the Δ 's are all zero. The Δ_n's represent the dimensionless residuals in the constraint equations at the n'th iteration. It is desired to

relax the selected functions to zero by the Newton-Raphson method of linearized differential corrections, i.e.,

$$0 = \Delta^{p}_{n} + \left(\frac{\partial \Delta^{p}_{n}}{\partial T}\right) \delta T_n + \left(\frac{\partial \Delta^{p}_{n}}{\partial \lambda^{\beta}}\right) \delta \lambda^{\beta}_{n} \qquad (25a.)$$

$$0 = \Delta^{\alpha}_{n} + \left(\frac{\partial \Delta^{\alpha}_{n}}{\partial T}\right) \delta T_n + \left(\frac{\partial \Delta^{\alpha}_{n}}{\partial \lambda^{\beta}}\right) \delta \lambda^{\beta}_{n} \qquad (25b.)$$

It should be noted in passing that the Δ^{α} 's could also be formulated from equation 21 as

$$\frac{H}{N^{\alpha}} \frac{\langle \omega^{\alpha} \rangle}{\langle \hbar \rangle} - 1$$

and still retain the non-dimensionality.

The δT_n and $\{\delta \lambda^{\alpha}_{n}\}$ represent the first order corrections to T and $\{\lambda^{\alpha}\}$ respectively to obtain the desired zeros. From this point on the dummy subscript/superscript β shall imply a general atomic species $1 \leq \beta \leq A$. The various partial derivatives are evaluated at parameter values appropriate to the n'th estimate. The first order corrections are determined by the inversion of the resulting A + 1 linear simultaneous relations.

The partial derivatives are obtained from the defining relations of the Δ 's,

$$\frac{\partial \Delta^{p}}{\partial T} = \frac{\partial}{\partial T}\left[\langle 1 \rangle - 1\right] = \frac{\langle \hbar \rangle}{RT^2} \qquad (26a.)$$

$$\frac{\partial \Delta^{p}}{\partial \lambda^{\beta}} = \frac{\partial}{\partial \lambda^{\beta}}\left[\langle 1 \rangle - 1\right] = \frac{\langle \omega^{\alpha} \rangle}{R} \qquad (26b.)$$

$$\frac{\partial \Delta^{\alpha}}{\partial T} = \frac{\partial}{\partial T}\left[\frac{N^{\alpha}\langle \hbar \rangle}{H \langle \omega^{\alpha} \rangle} - 1\right] = \frac{N^{\alpha}}{H}\left[\frac{\langle \hbar^2 \rangle}{R \langle \omega^{\alpha} \rangle T^2} + \frac{\langle c_p \rangle}{\langle \omega^{\alpha} \rangle} - \frac{\langle \hbar \rangle \langle \omega^{\alpha} \hbar \rangle}{\langle \omega^{\alpha} \rangle^2 RT^2}\right] \qquad (26c.)$$

$$\frac{\partial \Delta^{\alpha}}{\partial \lambda^{\beta}} = \frac{\partial}{\partial \lambda^{\beta}}\left[\frac{N^{\alpha}\langle h\rangle}{H} - 1\right] = \frac{N^{\alpha}}{H}\left[\frac{\langle h\, w^{\beta}\rangle}{R\langle w^{\alpha}\rangle} - \frac{\langle h\rangle}{\langle w^{\alpha}\rangle^{2}}\frac{\langle w^{\alpha} w^{\beta}\rangle}{R}\right] \qquad (26d.)$$

The various averages are computed using the partial pressures predicted by equation 23 with the n'th estimates. Substituting the derivatives of equations 26 into equation 25 and transposing the constants results in equation 27.

$$-\Delta^{p}_{n} = \frac{\langle h\rangle_{n}}{RT_{n}}\frac{\delta T_{n}}{T_{n}} + \langle w^{\beta}\rangle_{n}\frac{\delta \lambda^{\beta}_{n}}{R} \qquad (27a.)$$

$$-\Delta^{\alpha}_{n} = \frac{N^{\alpha}RT_{n}}{H\langle w^{\alpha}\rangle_{n}}\left[\frac{\langle c_{p}\rangle_{n}}{R} + \frac{\langle h^{2}\rangle_{n}}{R^{2}T_{n}^{2}} - \frac{\langle h\rangle_{n}\langle w_{\alpha} h\rangle_{n}}{\langle w^{\alpha}\rangle_{n} R^{2}T_{n}^{2}}\right]\frac{\delta T_{n}}{T_{n}} \qquad (27b.)$$

$$+ \frac{N^{\alpha}}{H\langle w^{\alpha}\rangle_{n}}\left[\langle h\, w^{\beta}\rangle_{n} - \frac{\langle h\rangle_{n}}{\langle w^{\alpha}\rangle_{n}}\langle w^{\alpha} w^{\beta}\rangle_{n}\right]\frac{\delta \lambda^{\beta}}{R}$$

Upon inverting this system, the parameters for the (n + 1)'st estimate are arrived at by adding the corrections to the n'th estimates, i.e.,

$$\{\lambda^{\beta}_{n+1}\} = \{\lambda^{\beta}_{n}\} + \{\delta\lambda^{\beta}_{n}\} \qquad (28a.)$$

$$T_{n+1} = T_{n}\exp\frac{\delta T_{n}}{T_{n}} \qquad (28b.)$$

The exponential form of T is selected to insure only positive temperatures. In the limit of small values of $\delta T_n/T_n$ this reduces to simple additivity of the linear correction. The exponential dependence of p_1 upon $\{\lambda^{\alpha}\}$ guarantees the non-negativity of pressure.

The linearized iteration scheme described in the preceeding will succeed in converging to the equilibrium solution only so long as the influence of the truncated terms

of the series expansion remain small. This may not always be the case, and is the subject of a succeeding section.

Part IV

THE STABILITY OF THE EQUILIBRIUM STATE

In order to establish that the optimized solution is a maximum, the entropy function must be concave in the region. This requires that, for a virtual displacement of the system from the converged solution, the first order change of entropy must be zero and the second order change must be negative. To evaluate the second order change it is necessary to return to the constrained optimum problem. Consider an optimizing function

$$\phi' = S - \psi H + \sum_{\alpha} \lambda^{\alpha} N^{\alpha} \tag{29}$$

where $\{\lambda^{\alpha}\}$ are the Lagrange multipliers for the atomic specie constraints and ψ the multiplier for the constrained enthalpy. The constraint equations are as follows,

$$P = P \tag{30a.}$$

$$H = \sum_{i} N_i h_i \tag{30b.}$$

$$\{N^{\alpha}\} = \left\{\sum_{i} N_i \omega_i^{\alpha}\right\} \tag{30c.}$$

Given the entropy function in terms of temperature, pressure, and mole numbers for a mixture of perfect gases, i.e. equation 31,

$$S = \sum_{i} \frac{N_i h_i}{T} - \sum_{i} \frac{N_i \mu_i^{+}}{T} - NR \ln\left(\frac{P}{p^{+}}\right) - \sum_{i} N_i R \ln N_i + NR \ln N \tag{31}$$

the ϕ' function may be expressed explicitly.

$$\phi' = \sum_i \frac{N_i h_i}{T} - \sum_i \frac{N_i \mu_i^+}{T} - NR \ln (P/p^+) - \sum_i N_i R \ln N_i \qquad (32)$$
$$+ NR \ln N - \psi \sum_i N_i h_i + \sum_\alpha \sum_i \lambda^\alpha N_i \omega_i^\alpha$$

To a quadratic approximation, the variation in ϕ' is given by (33)

$$\delta\phi' = \sum_i N_i c_{p_i} \left(\frac{1}{T} - \psi\right) + \sum_i \left[h_i \left(\frac{1}{T} - \psi\right) + \omega_i^\alpha \lambda^\alpha - \frac{\mu_i^+}{T}\right.$$
$$\left. - R \ln (P/p^+) + R \ln N - R \ln N_i\right] \delta N_i$$

$$- \sum_i \frac{N_i c_{p_i}}{2} \left(\frac{\delta T}{T}\right)^2 + \sum_i c_{p_i} \left(\frac{1}{T} - \psi\right) \delta T \, \delta N_i$$

$$+ \frac{R}{2} \frac{(\delta N)^2}{N} - \frac{R}{2} \sum_i \frac{(\delta N_i)^2}{N_i}$$

Applying the principle that the first order variations must be independently zero, the previously formulated equilibrium conditions are repeated, i.e.,

$$\sum_\alpha \lambda^\alpha \omega_i^\alpha = +\mu_i/T$$

$$S_{max} = \frac{H}{T} - \sum_\alpha \lambda^\alpha N^\alpha$$

and the Lagrange multiplier ψ becomes the inverse of temperature. The quadratic variation must be negative in sum, if the optimized state is truly a maximum. The remaining quadratic terms of the variation, therefore, must obey the inequality of equation 34.

$$\frac{(\delta N)^2}{N} - \sum_i \frac{(\delta N_i)^2}{N_i} < \sum_i \frac{N_i c_{p_i}}{R} (\delta \ln T)^2 \qquad (34)$$

The mole numbers may be eliminated from equation 34 by applying equation 19 and its variation. The substitution into equation 34 produces the new inequality of equation 35.

$$\sum_i \frac{p_i}{P}\left[\frac{c_{p_i}}{R}(\delta \ln T)^2 + 2\frac{\delta N}{N}\frac{\delta p_i}{p_i} + \left(\frac{\delta p_i}{p_i}\right)^2\right] > 0 \tag{35}$$

The inequality of equation 35 may be cast in terms of the element potentials by substituting from the variation of equation 18, i.e.,

$$\frac{\delta p_i}{p_i} = \langle \omega_i^{\beta} \rangle \frac{\delta \lambda^{\beta}}{R} + \frac{\langle h \rangle}{RT}\delta \ln T \tag{36}$$

and noting that, in equilibrium, the number of moles may be expressed in terms of the enthalpy as follows

$$N = H/\langle h \rangle \tag{37}$$

therefore:

$$\frac{\delta N}{N} = -\frac{\delta \langle h \rangle}{\langle h \rangle} = -\frac{\langle c_p \rangle}{\langle h \rangle}\delta T - \sum_i \frac{\delta p_i}{p_i}\frac{h_i}{\langle h \rangle} \tag{38}$$

The result of the substitution is presented in equation 39.

$$\langle \omega^{\alpha}\omega^{\beta} \rangle \frac{\delta \lambda^{\alpha}}{R}\frac{\delta \lambda^{\beta}}{R} > 2\langle \omega^{\alpha} h \rangle \frac{N^{\beta}}{H}\frac{\delta \lambda^{\alpha}}{R}\frac{\delta \lambda^{\beta}}{R} \tag{39}$$

$$+ \delta \ln T\left[\frac{\langle c_p \rangle}{R} + \frac{\langle h^2 \rangle}{R^2 T^2}\right]\left[\delta \ln T + \frac{2N^{\alpha}RT}{H}\frac{\delta \lambda^{\alpha}}{R}\right]$$

The inequality of equation 39 is of value in determining whether a given set of parameter estimates will readily converge to the equilibrium values upon the application of

a linearized iteration technique, since it contains the thermodynamic constraint upon second variations.

If the linearized corrections to the solution parameters $\{\chi\}$, T do not satisfy equation 39, it is apparent that the starting estimates were made in a region of the variable space that does not possess the correct curvature to describe a maximum. It may be more efficient to re-estimate than to extrapolate from the initial point, for the entropy surface may not be amenable to a linear fit when far from equilibrium. The coefficients of equation 39 should be evaluated at the equilibrium condition. This is not known a priori, and the estimated properties must be substituted. This lessens the effectiveness of equation 39 as a calculation aid. However, this is a good a posteriori check of the estimate method developed. A further discussion of this point is presented in Part VI when numerical results are compared.

Part V

CONVERGENCE OF THE SOLUTION

The application of a linearized iterative technique cannot guarantee unconditional convergence to the equilibrium solution. The thermodynamic stability criterion discussed in Part IV is a convenient discriminator for first estimates and gives an indication of the thermodynamic influence upon solution convergence, but is admittedly cumbersome for evaluation at each step. It is convenient to introduce some measure of the total error in the solution to judge the progress of successive iterations and determine when the solution has essentially converged. This can reduce the number of iterations to convergence by indicating the most efficacious path of relaxation. In the linearized scheme, the slopes of the Δ functions are extended in the various coordinate directions from the estimated point. Due to curvature of the function, the linear extension departs from the true dependence. Because of this departure it may be expected that the direction of the change is approximately correct, but that the magnitude of the correction vector may be incorrect. If the proposed linearization is a good estimate of the actual dependence, the optimum correction vector magnitude will approach the predicted magnitude. The optimum magnitude is that which minimizes the errors Δ^p and $\{\Delta^\alpha\}$. The Δ^p and $\{\Delta^\alpha\}$ are dimensionless measures of the errors in the various constraints, are zero in equilibrium, and are

normalized. The normalization permits comparison of the errors with unity to determine an absolute measure of convergence.

The optimization is a one-dimensional one resulting in the proportion of the predicted correction magnitude which results in the minimum error. A logical choice for the error function to be minimized is the sum of the squares of the Δ^{p} and $\{\Delta^{\alpha}\}$. Define the error at the n'th iteration to be

$$E_n^2 \equiv \left(\Delta_n^p\right)^2 + \sum_{\alpha}' \left(\Delta_n^{\alpha}\right)^2 \tag{40}$$

If the iterative scheme is to be convergent, subsequent errors should be monotonically decreasing, i.e., $E^2_{n+1} < E^2_n < E^2_{n-1}$. After inverting the correction matrix for the n'th iteration one obtains the linear corrections $\delta \ln T_n$ and $\delta\lambda_n^{\beta}$. The parameters to be used to calculate the properties at the n + 1'st iteration are therefore

$$\lambda^{\beta}_{n+1} = \lambda^{\beta}_n + \pi_n \, \delta\lambda^{\beta}_n \tag{41a.}$$

$$T_{n+1} = T_n \left[1 + \pi_n \, \delta \ln T_n\right] \tag{41b.}$$

In order to minimize the number of iterations required, it is desirable to select π_n such that the error at the start of the n + 1'st iteration is a minimum. This requires the one dimensional optimization of E^2_{n+1} with respect to π_n, where

$$E^2_{n+1} = \left[\Delta^p\left(\lambda^{\beta}_n + \pi_n \delta\lambda^{\beta}_n\right);\ T_n\left[1+\pi_n\,\delta \ln T_n\right]\right]^2 \qquad (42)$$

$$+\left[\Delta^{\alpha}\left(\lambda^{\beta}_n + \pi_n \delta\lambda^{\beta}_n\ ;\ T_n\left[1+\pi_n\,\delta \ln T_n\right]\right)\right]^2$$

This implicit function of π_n is most easily optimized by a graphical determination. For each value of π_n, the function must be evaluated. After each iteration this optimization must be repeated. The number of iterations, and therefore, the number of matrix inversions, may be reduced at the expense of more matrix multiplications and manipulations. This inconvenience can be minimized by recognizing that the optimization need be only approximate. The important criterion is that the subsequent error E^2_{n+1} be smaller than E^2_n. Therefore, if one evaluates E^2_{n+1} for $\pi_n = 1$, assuming the linear correction technique to be exact, and finds it less than E^2_n, the convergence is assured and the next iteration may be started. Note that the components Δ^p and Δ^{α} must be computed for the next iteration matrix anyway. If E^2_{n+1} ($\pi_n = 1$) is not less than E^2_n, then one may select other values of π_n and determine the corresponding error. A choice of $\pi_n = 0.5$ will give a third point, and the trend of E^2_{n+1} should be apparent, at least in approximation.

It must be noted that, although the errors Δ^p and Δ^{α} are dimensionless they may have a disproportionate influence upon the combined error E^2. In particular, the enthalpy terms in Δ^{α}, i.e., $\langle R \rangle / H$

The enthalpy is a relative property. A gas mixture may, depending upon the datum selected, possess either a negative or a positive value of H. This may "sensitize" the error function to small changes in enthalpy since, for small changes in parameters, $\frac{\langle h \rangle}{H}$ can undergo order of magnitude changes as well as sign changes. One could, with sufficient substantiating experience, assign weighting coefficients in the error function formulation to account for these inequities and define an error function of the type

$$E^{*2} \equiv \left(\Delta^{p}\right)^2 + \sum_{\alpha} \Gamma_{\alpha} \left(\Delta^{\alpha}\right)^2 \tag{43}$$

It will be demonstrated numerically that the selection of the enthalpy base implicitly defines such a biasing. The enthalpy base which permits negative as well as positive values and has its zero in the range such that H is small in magnitude represents the most discriminating one with respect to enthalpy errors.

The iterative method fails for H = 0, due to the singularity introduced in the definition of Δ^{α}. Although such instances are rare, this dependence upon the enthalpy datum is somewhat disconcerting. It is generally accepted that one may assign an arbitrary datum for enthalpy measurement. However, the present difficulty is primarily one of definitions. In Part IX a more fundamental problem with respect to the enthalpy datum arises and is discussed briefly.

Part VI

APPLICATION OF THE ELEMENT POTENTIAL METHOD TO THE EQUILIBRIUM DETERMINATION OF THE NITROGEN TETROXIDE-HYDRAZINE COMBUSTION SYSTEM

To demonstrate the application of the calculation method described, a typical solution is presented. The chemical system selected is that of nitrogen tetroxide (N_2O_4) and hydrazine (N_2H_4) in a mass mixture ratio (O/F) of 1.2:1. The combustion is assumed to occur at 150 psia. This system is a convenient example in that the equilibrium solution is available from independent calculations for comparison purposes. From these assumptions, and the properties of the reactants, the $\{N^\alpha\}$ and H may be determined as follows: The masses of the separate reactants are

$$\text{mass of } N_2H_4 = \frac{1}{1 + 1.2} = 0.4545 \text{ gr./gr. mixture}$$

$$\text{mass of } N_2O_4 = \frac{1.2}{1 + 1.2} = 0.5455 \text{ gr./gr. mixture}$$

The moles of reactants are computed, using the molecular weights of the reactants, to be

$$\text{moles of } N_2H_4 = \frac{0.4545}{32.048} = 0.014183 \text{ mol./gr. mixture}$$

$$\text{moles of } N_2O_4 = \frac{0.5455}{92.016} = 0.005928 \text{ mol./gr. mixture}$$

Using the chemical formulae for the reactants, the gram atoms of the species $\{N^\alpha\}$ are

$N^H = 4(0.014183) = 0.05673$ gr. at./gr. mixture

$N^N = 2(0.014183) + 2(0.005928) = 0.04022$ gr.at./gr. mixture

$N^O = 4(0.005928 = 0.02371$ gr. at./gr. mixture

The mixture enthalpy is determined from the assigned enthalpy* of the reactant mixture at the input conditions (298° K assumed)

$h(N_2O_4) = -.578$ Kcal./mol.

$h(N_2H_4) = 18.170$ Kcal./mol.

$H = (0.005928)x(-.578) + (0.014183)x(18.17) = .2543$ Kcal./gr. mixture

$= 254.3$ cal./gr. mixture

This completes the determination of the equilibrium constraints.

The first estimate of combustion temperature is selected to be 2500° K., approximately 500 K° less than the established equilibrium value[9] This was selected as being representative of the uncertainty in temperature of an unexplored system. Appendix I contains the method of determining the first estimates of $\{\lambda^{\alpha}\}$ from the assumed temperature. The potentials are estimated to be,

$$\lambda_1^H/R = -9.91$$

$$\lambda_1^N/R = -12.92$$

$$\lambda_1^O/R = -18.06$$

*Unless otherwise specified, thermodynamic properties are taken from reference (8).

Using these values for the potentials at 2500° K, the vector of partial pressures of the molecular species is computed from equation 23. The various coefficients of equation 27 are evaluated using the partial pressure averaging technique. The resulting 4 simultaneous linear correction equations are then solved. The first order corrections are made to $\{\lambda^{\alpha}\}$ and T and a new composition vector computed. The results of the first three iterations are presented in Table I. The root of the error function ($\sqrt{E^2}$) and the function $\frac{H}{RT} - \sum_{\alpha} \lambda^{\alpha} \frac{N}{R}^{\alpha}$ are presented as well, the latter is identically the entropy (S/R) in the equilibrium state only. The parameters appropriate to the zero'th estimate, i.e., the elemental products estimate of Appendix I are presented to illustrate the relative accuracy of the initial estimate procedure.

Table I

RESULTS OF THE EQUILIBRIUM CALCULATION FOR THE COMBUSTION OF N_2O_4 - N_2H_4 AT 150 PSIA AND O/F = 1.2:1

	$\lambda H/R$	$\lambda N/R$	$\lambda O/R$	T (°K)	$\sqrt{E^2}$	$\frac{H}{RT} - \frac{\lambda^{\alpha} \tilde{N}}{R}$
Zero Estimate (elemental products)	-9.12	-13.03	-14.22	2500	715.0	1.430
First Estimate	-9.91	-12.92	-18.06	2500	3.50	1.560
1st Iteration						
Second Estimate	-9.63	-13.20	-18.00	2857	0.561	1.546
2nd Iteration						
Third Estimate	-9.97	-13.29	-17.14	2975	0.310	1.550
3rd Iteration						
Fourth Estimate	-10.10	-13.31	-16.84	3025	0.141	1.550
Independent Solution(9)	-10.21	-13.34	-16.58	3055	0	1.551

The results presented are for iterations in which the full first order corrections were applied. It is worthwhile to note that the error $\sqrt{E_n^2}$ is monotonically decreasing for this system. To determine any departure from the optimal iterative steps, the error was evaluated for intermediate cases, i.e., fractional first order corrections. In all cases, the linear step appeared to be approximately optimum. A solution using precisely optimum iteration steps was not performed. The results of this survey are presented in Table II, for the sample calculation at the first and second iterative step.

Table II

OPTIMIZATION OF THE ITERATIVE PATH

	$\pi n = 0$	$\pi n = 0.5$	$\pi n = 1$	$\pi n = 1.5$
$\sqrt{E_2^2}$	3.50	2.65	0.561	1.74
$\sqrt{E_3^2}$	0.561	0.270	0.310	--

These results point up the practical efficiency of using the full predicted step between iterations, provided that the error is decreasing.

In defining the error function (E^2), it was noted that the magnitude of the function is dependent upon the enthalpy base selected. The dependence of the magnitude of the error at the initial estimate upon the base selected has been determined for three enthalpy reference systems in common use. In (1) zero enthalpy is assigned to certain stable

compounds at 0° K such that virtually all other molecular species possess positive enthalpies. In (8) zero enthalpy is assigned to the elements at 0° K. In (10) the elements are assigned zero enthalpy at standard temperature (298° K). It is apparent that, in the order presented, the reference bases tend to smaller algebraic enthalpies for a given species.

The values of the mixture enthalpy computed from the prescribed reactant enthalpies for the iterative example are, 2224 cal./gr., 254.3 cal./gr. and 130.6 cal./gr. respectively, for the three enthalpy reference systems mentioned. The corresponding errors at the first iteration ($\sqrt{E_1^2}$) were 0.48, 3.50, and 8.18 respectively. This illustrates that the error function described can assume different values for the same estimate, depending upon the enthalpy reference. This scale change does not alter the normalization or dimensionality of the error function. It merely serves to accentuate small enthalpy errors.

In Part IV, the criterion for the stability of the equilibrium state was developed in element potential coordinates. For the example under investigation, equation 39 has been evaluated for several estimates of the solution parameters. The various coefficients of equation 39 can be evaluated from the known equilibrium state. For a given estimate, the displacements $\delta \ln T$ and $\{\delta\lambda^{\alpha}\}$ are determinable. Since the estimating procedure of Appendix I requires only the assumption of a trial temperature, the stability

criterion may be applied to determine the adequacy of the estimates at various levels of temperature error.

The equilibrium value of the temperature is 3055° K. The inequality of equation 39 was tested at 2000° K, 2500° K, 3500° K and 4000° K. The results indicate that the inequality is served at 2500° K and 3500° K but is violated at 2000° K and 4000° K. This implies that, for this problem, the estimating technique places the parameters in the region of the equilibrium state if the temperature estimate is in error by less than approximately 500 K°. The preceeding is substantiated by noting that at 2500° K the solution converged readily without recourse to any damping of the linearized scheme. This was not the case for an attempted solution using the elemental products estimate.

Part VII

AN ESTIMATE OF TRACE MOLECULAR SPECIES AND A TEST FOR CONDENSED PHASES

The analysis presented will determine the equilibrium state of maximum entropy for a specified set of molecular species assumed to be present in the mixture. For the sake of brevity, only a portion of the possible molecular species are considered in the equilibrium determination because of the vanishingly small mole fractions, and therefore influence, of certain molecular forms in a given region of temperature. The rank of the correction matrix is unaffected by the number of molecular species considered. However, the vector multiplications represented by the coefficients of the matrix become operationally more cumbersome to perform because of the number of components involved. This implies that an appreciable calculation effort may be expended needlessly by considering trace species. A procedure for avoiding this is described in the following.

At each step in the iteration, the mole fraction of all possible molecular species may be evaluated from the estimated parameters to be

$$\frac{p_i}{P} = \frac{N_i}{N} = \frac{p^+}{P} \exp\left[\frac{\lambda^\beta \omega_i^\beta}{\mathcal{R}} - \frac{\mu_i^+}{\mathcal{R}T} \right]$$

Those species exhibiting a value less than some arbitrary level, e.g. 10^{-4} to 10^{-5} should be neglected in the succeeding iteration. The correction matrix coefficients are computed

on the basis of a mole fraction average, and therefore coefficients computed for the truncated species distribution will assymptotically approach the values computed considering all possible species. At convergence, when the error has been reduced to an arbitrarily small value, the parameters $\{\lambda^{\alpha}\}$, T are assymptotically approaching the exact values, and the partial pressures of trace species predicted from these parameters are essentially correct. The resultant mismatch in constraints $\{N^{\alpha}\}$, H, P, should remain negligible. This mismatch may readily be determined if desired.

This procedure may be used to predict the presence of condensed phases as well, although only qualitatively at present. A gaseous molecular specie may represent the vapor phase of a possible condensed phase. Although only perfect gases have been considered in the iterative scheme, the underlying analysis is applicable to condensed phases. The chemical potential (μ_i) of the gaseous phase of a molecular species is, in the equilibrium state, equal to $T\sum_{\alpha}\lambda^{\alpha}\omega_i^{\alpha}$. The molal chemical potential of a pure, ideal condensed phase is only a function of temperature, and is tabulated. Therefore, if the value of the chemical potential of the condensed phase of molecule i at the converged temperature T is less than the gaseous phase potential computed from $T\sum_{\alpha}\lambda^{\alpha}\omega_i^{\alpha}$, the condensed phase is present in some unspecified amount, and the solution must be re-evaluated, taking into account the phase or phases predicted. This recomputation has not been developed in the present analysis.

Part VIII

EXTENSION TO PSUEDO-EQUILIBRIUM STATES

The analysis presented is valid for predicting the state of equilibrium obtained by a mixture of reacting gases given time for all kinetic processes to subside, or come into balance. In a dynamic process it may be desired to determine the psuedo-equilibrium state in which certain, or all, of the molecular species are "frozen" at specified molal levels not necessarily those of the maximum entropy state. The iterative scheme may be applied to such systems to determine the adiabatic temperature and unspecified molecular specie mole numbers. This requires the introduction of the new constraint(s) that N^{γ} shall be a constant equal to the specified value for the frozen components. Here γ is a dummy variable representing the frozen specie j. The composition vector ω_j^{α} is replaced by one which has a zero component for all but $\alpha=\gamma$, for which the component is unity. This specification increases the number of variables to be iterated by one for every added constraint. In effect, the frozen molecular species are treated as inert, irreducible atomic species. The effect of the additional constraints is to uncouple the correction equations, and results in numerous zeros in the correction matrix.

An interesting extension of the psuedo-equilibrium approach is to cases in which a molecular specie is limited to mole numbers greater than a specified value. In such

cases, the molecular specie in question is introduced both as a psuedo-inert atomic specie and as a conventional product. This requires the introduction of two composition vectors for a single molecule and is best handled in the calculation by assigning one or the other a dummy notation.

Part IX

EXTENDING THE SOLUTION

Once the equilibrium solution has been obtained for a set of constraints P, $\{N^{\alpha}/H\}$, it may be desired to determine the influence of small changes in these constraints upon the equilibrium state. In particular, the solution at another pressure or enthalpy may be desired. The linear correction equations represent a perturbation procedure for just such changes. The functions $\Delta^{p}, \{\Delta^{\alpha}\}$, defined as the error components in the iterative calculation take on values appropriate to the perturbed constraints. A solution of the resulting simultaneous equations determines the linear perturbation of the parameters $\{\lambda^{\alpha}\}$, T, and permits an approximation of the new equilibrium state. The new constraints P', $N^{\alpha}{}'$, H' prescribe the new values of the Δ's as follows.

The linearized perturbation equations are

$$0 = \Delta^{p'} + \delta\Delta^{p'} \tag{44a.}$$

$$0 = \{\Delta^{\alpha'}\} + \{\delta\Delta^{\alpha'}\} \tag{44b.}$$

The errors, or residuals, are to be made zero in the new equilibrium state. The $\Delta^{p'}, \{\Delta^{\alpha'}\}$ are defined using the new constraints, i.e.,

$$\Delta^{p'} = \langle 1\rangle' - 1 = \frac{P}{P'}\langle 1\rangle - 1 \tag{45a.}$$

$$\Delta^{\alpha'} = \frac{N^{\alpha'}}{H'} \frac{\langle h \rangle'}{\langle \omega^{\alpha} \rangle'} - 1$$

$$= \frac{P}{P'} \frac{P'}{P} \frac{N^{\alpha'}}{H'} \frac{\langle h \rangle}{\langle \omega^{\alpha} \rangle} - 1 = \frac{N^{\alpha'}}{H'} \frac{\langle h \rangle}{\langle \omega^{\alpha} \rangle} - 1 \qquad (45b.)$$

The necessary derivatives are the same as those computed in the iterative scheme, except that all of the primed constraints are substituted. The resulting perturbation equations are therefore

$$1 - \frac{P}{P'} \langle 1 \rangle = \langle \omega^{\beta} \rangle \frac{P}{P'} \frac{\delta \lambda^{\beta}}{R} + \frac{\langle h \rangle}{RT} \frac{P}{P'} \delta \ln T \qquad (46a.)$$

$$1 - \frac{N^{\alpha'}}{H'} \frac{\langle h \rangle}{\langle \omega^{\alpha} \rangle} = \frac{N^{\alpha'}}{H' \langle \omega^{\alpha} \rangle} \left[\langle h \omega_{\beta} \rangle - \frac{\langle h \rangle}{\langle \omega^{\alpha} \rangle} \langle \omega^{\alpha} \omega_{\beta} \rangle \right] \frac{\delta \lambda^{\beta}}{R} \qquad (46b.)$$

$$+ \frac{N^{\alpha'} RT}{H' \langle \omega^{\alpha} \rangle} \left[\frac{\langle c_p \rangle}{R} + \frac{\langle h^2 \rangle}{R^2 T^2} - \frac{\langle h \rangle}{\langle \omega^{\alpha} \rangle} \frac{\langle \omega^{\alpha} h \rangle}{R^2 T^2} \right] \delta \ln T$$

This set of equations may be simplified by noting that $\frac{P}{P'}$ may be factored, and that the following relations are appropriate at the point from which the perturbation is made

$$\langle 1 \rangle = 1$$

$$\frac{\langle \omega^{\alpha} \rangle}{\langle h \rangle} = \frac{N^{\alpha}}{H}$$

A further abbreviation is possible by noting that for small changes in the variables

$$\frac{P' - P}{P} \simeq \ln \frac{P'}{P}$$

$$1 - \frac{N^{\alpha'}/H'}{N^{\alpha}/H} \simeq - \ln \frac{N^{\alpha'}}{N^{\alpha}} + \ln \frac{H'}{H}$$

$$\delta \ln T = \ln \left(\frac{T'}{T} \right)$$

Including these simplifications and abbreviations into the perturbation equations yields

$$\ln \left(\frac{P'}{P} \right) = \langle \omega^\beta \rangle \frac{\delta \lambda^\beta}{R} + \frac{\langle h \rangle}{RT} \ln \left(\frac{T'}{T} \right) \tag{47a.}$$

$$-\ln \left(\frac{N^{\alpha'}}{N^\alpha} \right) + \ln \left(\frac{H'}{H} \right) = \left[\frac{N^\alpha}{H} \frac{\langle h \omega^\beta \rangle}{\langle \omega^\alpha \rangle} - \frac{\langle \omega^\alpha \omega^\beta \rangle}{\langle \omega^\alpha \rangle} \right] \frac{\delta \lambda^\beta}{R} \tag{47b.}$$

$$+ \left[\frac{N^\alpha}{H} \frac{RT}{\langle \omega^\alpha \rangle} \left(\frac{\langle c_p \rangle}{R} + \frac{\langle h^2 \rangle}{R^2 T^2} \right) - \frac{\langle \omega^\alpha h \rangle}{\langle \omega^\alpha \rangle} \right] \ln \left(\frac{T'}{T} \right)$$

The presence of the primed quantities in the correction matrix would constitute a second order correction in the solution, and consequently they have been replaced by the base values. All other second order terms have been dropped in the linearization. Also, retaining the primed quantities would require the re-evaluation of the correction matrix at each perturbation. By this method, the solution may be extended from a known point to obtain approximations of the parameters appropriate to the new equilibrium state for constraints P', H', $\{N^{\alpha'}\}$. Again it must be cautioned that the enthalpy base selection may influence the accuracy when working with H and/or H' nearly zero.

Two numerical examples have been evaluated to illustrate the application of such a perturbation technique. The variations with pressure of $\{\lambda^\alpha\}$, and T were computed

for the 1.2:1 mixture ratio, nitrogen tetroxide-hydrazine system. These were compared with the values obtained by an independent exact solution.(9) The base point was at a pressure of 150 psia. The comparison was made for pressures from 5 psia to 160 psia. Further data for comparison was not conveniently available. The Δ^{α}'s are zero, since enthalpy and atomic specie values are constant, i.e., $H = H'$, $\{N^{\alpha}\} = \{N^{\alpha}{}'\}$. The influence of a pressure change appears only in the $\Delta p'$, which takes on the value $\ln \frac{P'}{P}$. The averaged properties at the base point of the perturbation are all available from the previously mentioned iterative solution. The set of perturbation relations were solved for the influence of pressure changes, and compared with the exact solution. The plots of $\{\lambda^{\alpha}\}$, T versus ln P for the exact solution are presented in Figures (1) and (2) respectively, and the slopes compared with those predicted by the perturbation method. The results of the slope comparison are presented in Table III.

Table III

COMPARISON OF THE PERTURBED SOLUTION AND AN EXACT CALCULATION FOR N_2O_4 - N_2H_4 COMBUSTION (O/F = 1.2:1)

	$\frac{d(\lambda^H/R)}{d\ln P}$	$\frac{d(\lambda^N/R)}{d\ln P}$	$\frac{d(\lambda^O/R)}{d\ln P}$	$\frac{d\ln T}{d\ln P}$
Perturbed	0.4128	0.4425	0.322	0.03035
Exact(9)	0.4213	0.4385	0.295	0.02915
% error	-2.0	0.87	9.1	4.1

THE VARIATION OF THE ELEMENT POTENTIALS WITH PRESSURE FOR N_2O_4-N_2H_4 COMBUSTION

$O/F = 1.2 : 1$

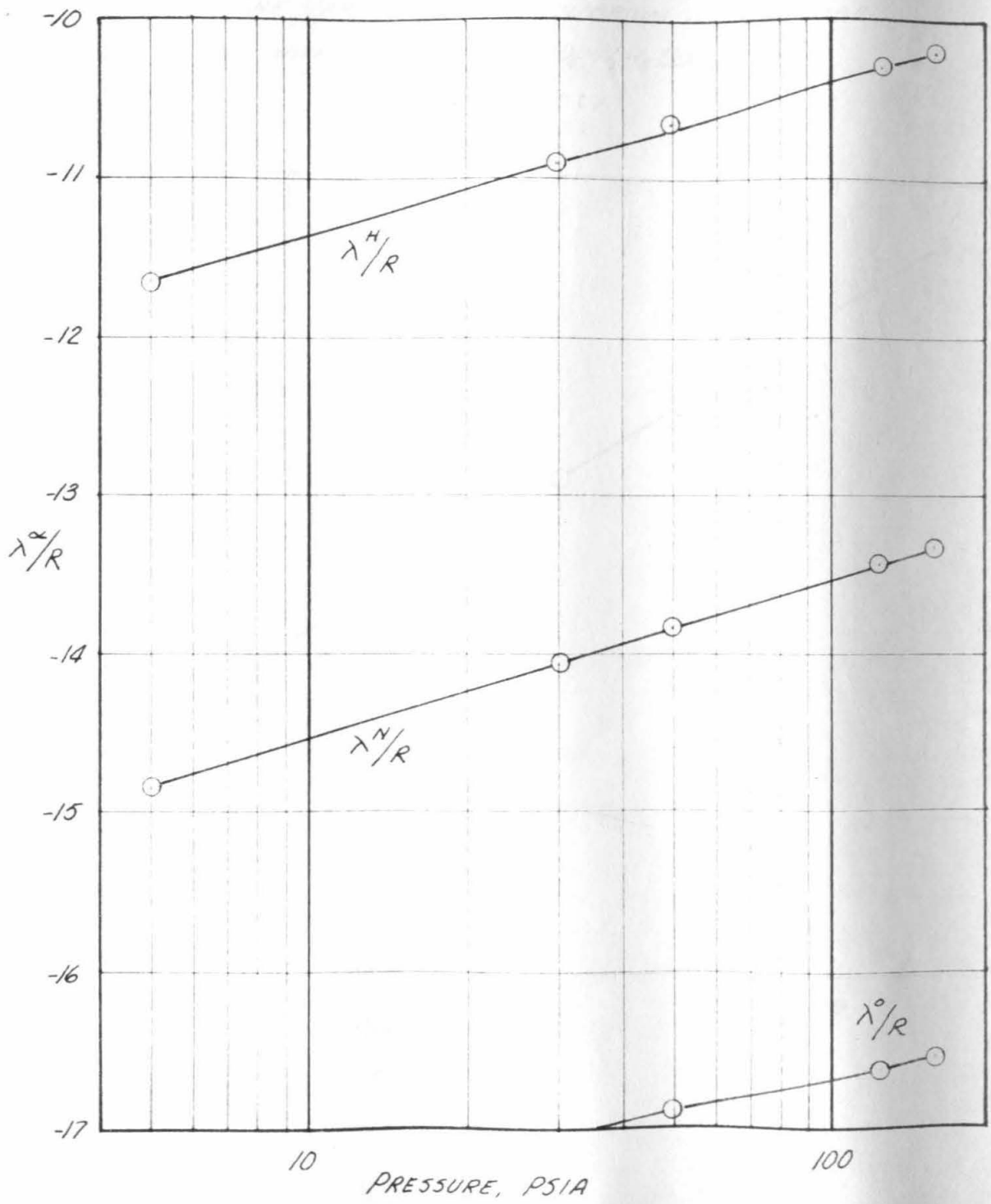

Figure 1

THE VARIATION OF EQUILIBRIUM TEMPERATURE WITH PRESSURE FOR N_2O_4-N_2H_4 COMBUSTION

O/F = 1.2 : 1

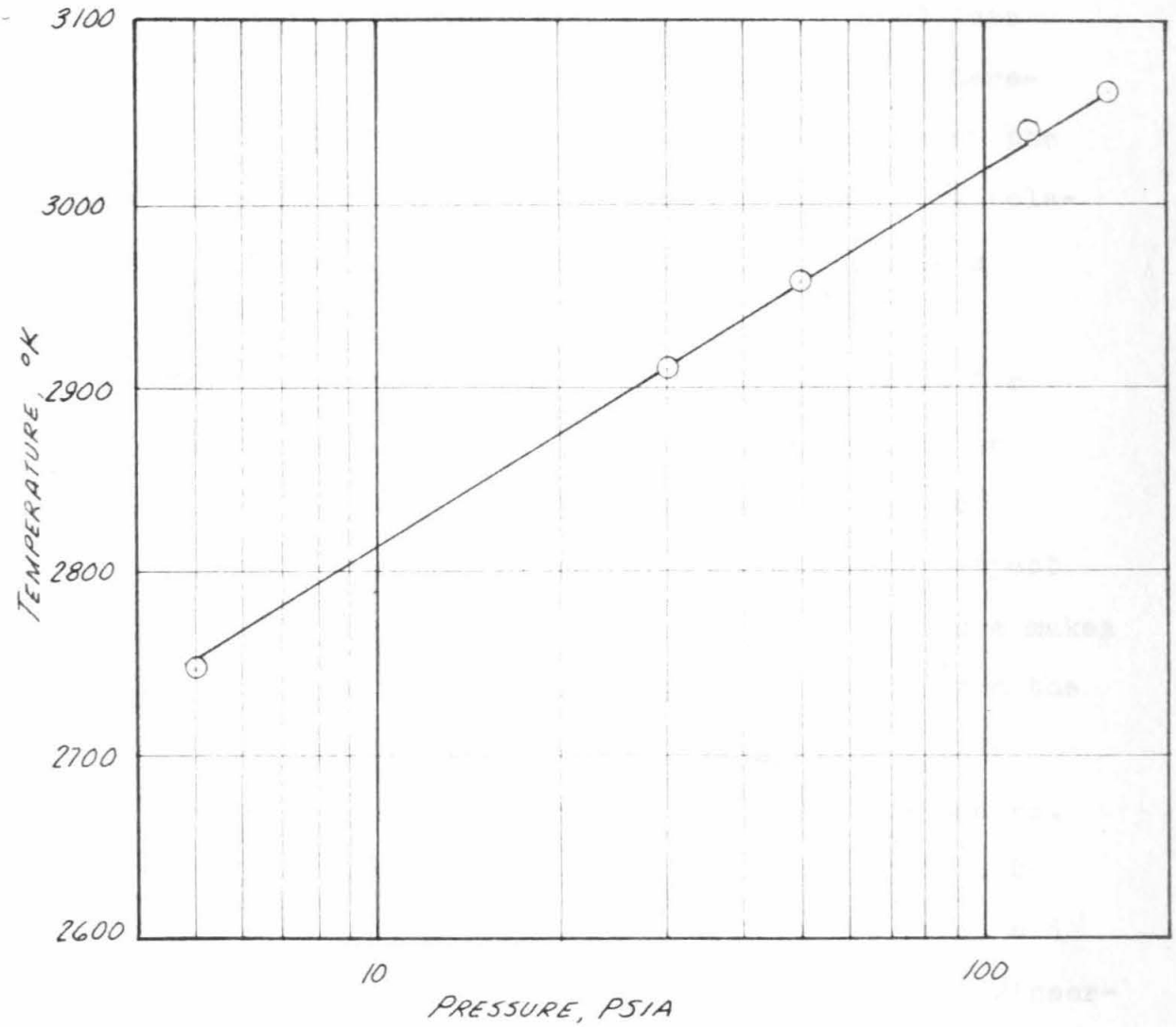

Figure 2

An examination of the plots of the exact solution parameters illustrates that only the parameter ln T deviates from a linear function of ln P over the range illustrated. The errors in the $\{\lambda^{\alpha}\}$ function slopes of Table III can be attributed to numerical inaccuracies in the correction matrix coefficients, and to the difficulty of establishing an accurate slope from the discreet points of the exact solution. The exact solution compared does not result directly in the element potentials, and therefore requires an intermediate calculation to arrive at the comparable variables. This calculation requires interpolation from the free energy (μ_i) tables at the various temperatures.

The success in predicting the equilibrium state for lower pressures than the base point implies that higher values should be equally successful since, for perfect gases, there can be no discontinuous behavior with respect to pressure. The perturbation with respect to pressure makes possible the examination of the effect of pressure upon the equilibrium without the necessity of repeating a multi-stepped iterative solution from arbitrary first estimates. For the specific example, the perturbation is shown to be valid over a considerable range (5 psia $<$ P' $<$ 160 psia) and may, in fact, be adequate over the range of general engineering interest in combustion processes.

The variation of the equilibrium state with a change of the applied pressure, as discussed in the preceding

paragraphs, is of considerable interest and may be examined further. If we assume that the perturbation is valid over some arbitrary range of pressure for fixed H, $\{N^{\alpha}\}$, the changes of the mole fractions of the mixture molecular components with pressure are easily predicted, since for a given species i

$$\frac{d\ln p_i}{d\ln P} = \omega_i^{\beta}\frac{d\lambda^{\beta}}{R\,d\ln P} + \frac{h_i}{RT}\frac{d\ln T}{d\ln P} \tag{48}$$

in the region in which the perturbation is valid. Denoting the new state with primes, this predicts that

$$\frac{p_i'}{P'} = \frac{p_i}{P}\cdot\left(\frac{P'}{P}\right)^{k_i-1} \tag{49}$$

for each molecular specie. The temperature for the new equilibrium state is given by

$$\left(\frac{T'}{T}\right) = \left(\frac{P'}{P}\right)^{k_T} \tag{50}$$

The k_i and k_t are all specified by linear combinations of the computed $\{\lambda^{\alpha}\}$, T slopes. The above forms would be of considerable value for instances in which a range of pressure levels is to be explored for a given set of constraints $\{N^{\alpha}\}$, H. For additional accuracy, an iteration at the new point would account for the higher order terms dropped.

One would expect that the most direct method of obtaining the variation of the solution parameters with pressure

would be through the differentiation of equation 22. Doing so results in the following,

$$\frac{d\lambda^{\beta}}{R\, d\ln P} = \frac{1}{\langle w^{\beta} \rangle}$$

$$\frac{d\ln T}{d\ln P} = \frac{RT}{\langle h \rangle}$$

A comparison of these predictions with the exact solution has been made for the sample calculation. The results are in poor agreement. The disagreement appears to be due to the relative nature of the enthalpy discussed previously. For instance, in the temperature derivative the variation of absolute temperature with absolute pressure is predicted to be a function of the relative property $\langle h \rangle$.

It was not convenient to evaluate the enthalpy perturbation solutions independent of any atomic specie changes because the exact solutions readily available are for constraint appropriate to the combustion of specific reactants. To compare, the perturbation was applied to the conditions of 1.0:1 and 1.6:1 mixture ratio combinations of nitrogen tetroxide and hydrazine at 150 psia. The base point for the perturbation was at 1.2:1 mixture ratio. These examples span the stoichiometric condition of 1.44:1. The magnitude of the perturbed constraints, the predicted values of the parameters, and the exact values are presented in Table IV.

Table IV

RESULTS OF A PERTURBATION IN MIXTURE RATIO FOR NITROGEN TETROXIDE-HYDRAZINE AT 150 PSIA

Mixture Ratio (O/F)	1.0:1	1.2:1	1.6:1
d log N^H/H	0.0023	0	-.00448
d log N^N/H	0.0514	0	-.0955
d log N^O/H	0.1845	0	-.339
pred. λ^H/R	-9.90	-	-10.70
exact λ^H/R	-9.85	-10.21	-10.71
pred. λ^N/R	-13.29	-	-13.41
exact λ^N/R	-13.28	-13.34	-13.36
pred. λ^O/R	-17.27	-	-15.36
exact λ^O/R	-17.53	-16.58	-15.53
pred. T^o K	2984	-	3157
exact T^o K	2945	3055	3059

The contents of Table IV illustrate that the results of the perturbation compare favorably with the exact solution values. Due to the rather large perturbation at the 1.6:1 point, the results deviate quantitatively from the exact values. In general, one will be interested in only small changes in constraints such as those that occur due to finite heat transfer or limited secondary injection.

Expression of the equilibrium state in terms of the element potentials for gaseous systems permits a considerable reduction in calculation effort when a number of conditions are to be investigated for a given set of reactants. At a given pressure, the converged iteration for a specified mixture ratio represents a base point for a perturbation to other mixture ratios. If not exact, this at least will give adequate estimates for rapid convergence at the new point. Given results at one pressure, the perturbation procedure determines the equilibrium state for other pressures without subsequent iteration. Since the iterative process is usually the most time-consuming calculation in thermochemical problems, the potential computational savings is considerable. The parameters $\{\lambda^{\alpha}\}$, T were determined from the exact solution[9] of the nitrogen tetroxide-hydrazine combustion system. They are presented in Table V, and illustrated graphically in Figure (3). A tabulation of the $\{\lambda^{\alpha}\}$ and T as a function of $\{N^{\alpha}\}$, H, and P from the results of completed solutions could aid in

estimating parameters appropriate to different constraints. In this regard, a correlation formula might be developed to speed the estimating.

Table V

SPECIFICATION OF THE EQUILIBRIUM STATE FOR NITROGEN TETROXIDE HYDRAZINE COMBUSTION AT 150 PSIA

$0.3 < (O/F) < 3.0$

O/F	N^H/H^*	N^N/H^*	N^O/H^*	λ^H/R	λ^N/R	λ^O/R	T(°K)
0.3	2.209×10^{-4}	1.220×10^{-4}	0.231×10^{-4}	- 8.41	-12.33	-25.41	1757
0.5	2.213×10^{-4}	1.299×10^{-4}	0.386×10^{-4}	- 8.96	-12.75	-21.59	2221
1.0	2.226×10^{-4}	1.500×10^{-4}	0.775×10^{-4}	- 9.85	-13.28	-17.53	2945
1.2	2.231×10^{-4}	1.582×10^{-4}	0.932×10^{-4}	-10.21	-13.34	-16.58	3055
1.6	2.241×10^{-4}	1.745×10^{-4}	1.245×10^{-4}	-10.71	-13.35	-15.53	3059
3.0	2.277×10^{-4}	2.328×10^{-4}	2.380×10^{-4}	- 8.22	-13.07	-21.41	2633

*Units are gr. atoms/cal.

VARIATION OF THE SOLUTION PARAMETERS WITH MIXTURE RATIO FOR N_2O_4 - N_2H_4 COMBUSTION

P = 150 psia

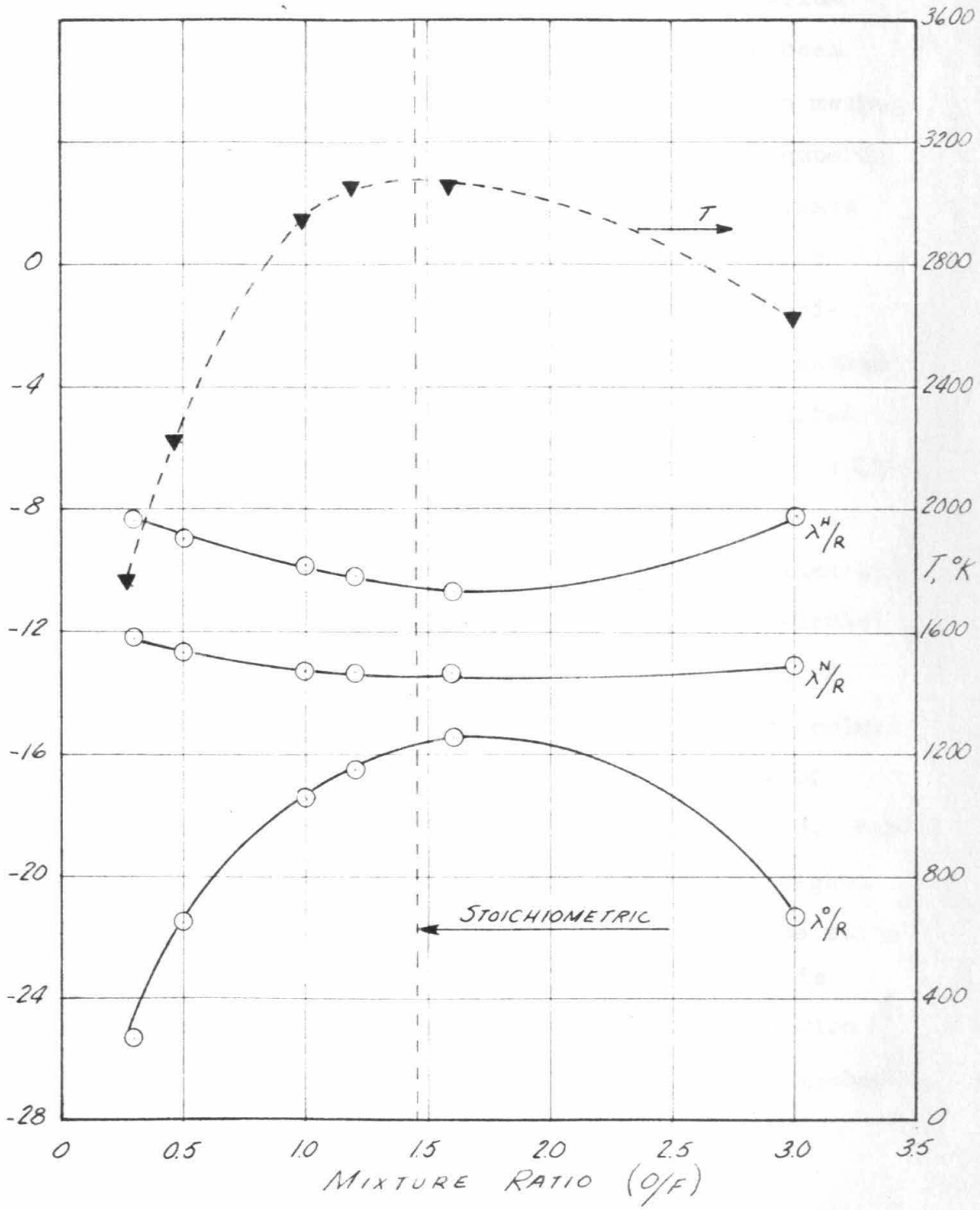

Figure 3

Part X

CONCLUSIONS

The presented method of determining the equilibrium state of a mixture of chemically reacting gases has been shown to be simple and versatile in application. The method of determining starting values from an estimate of temperature alleviates the chore of making an arbitrary estimate of the many variables involved, and at the same time it results in an accurate starting point. A stability criterion for the equilibrium state is presented in the element potential coordinates. The perturbation method presented is valuable in determining the trend of the solution resulting from a change in constraints, without resorting to a detailed exact solution. Some, or all, of these refinements could be advantageously incorporated into existing calculation programs to reduce the time, and therefore cost, of digital computer operation for propellant performance calculations. The iterative solution deals with a number of equations equal to the number of atomic types plus one. For typical calculations this number will rarely exceed eight. Therefore, limited capacity computing equipment may be utilized in the analysis. The error criterion discussed is useful as a solution aid and may find further application in a study of the convergence limits of the solution method presented.

NOMENCLATURE

Symbols

A	Number of atomic species in the mixture
A^{α}	Atomic weight of atomic species α
C	Number of molecular species in the gaseous mixture
C_p	Molal specific heat at constant pressure
E^2	Error function of equation 40
F	Gibbs function (H-TS)
H	Mixture enthalpy
h	Molal enthalpy
N	Number of moles
P	Total hydrostatic pressure
p_i	Partial pressure of component i
R	Molal perfect gas constant
S	Mixture entropy
T	Thermodynamic temperature
U	Mixture internal energy
V	Mixture total volume
$\triangle$	Iterative function, equation 24
ϕ, ϕ'	Optimizing functions, equations 7, 29
λ	Element chemical potential
ω	Stoichiometric coefficient
μ	Molal chemical potential

Operators

d, ∂	Differential
δ	Finite difference

$\langle\ \rangle$ Average by mole fraction

$\{\ \}$ A vector of components

Subscripts/Superscripts

α Pertaining to atomic type α

β General atomic type

i Pertaining to molecular specie i

n Denoting the n'th estimate in the iterative solution

' Denoting the perturbed values of the system constraint

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Appendix I

A METHOD FOR DETERMINING STARTING ESTIMATES

It has been stated that accurate first estimates of the parameters $\{\lambda^{\alpha}\}$ were simple to evolve. The succeeding is a technique for obtaining these estimates. The first estimate of temperature is strictly an estimate, in that no simple approximation technique appears applicable. In lieu of any intuitive feeling, some standard estimate may be used. The values of $\{\lambda_1^{\alpha}\}$ can be estimated from the assumed temperature and the system constraints. Due to the additivity of the atomic potentials to result in molecular potentials, as described in equation 11, it is not necessary to estimate the chemical potentials of monatomic species. One need only estimate the chemical potential of A molecular species which have linearly independent composition vectors (ω_i^{α}). Thus one selects components, one representative of each atomic species present.

The initial estimates of the $\{\lambda^{\alpha}\}$ are arrived at by the solution of the A equations,

$$\frac{\lambda_1^{\beta}\omega_i^{\beta}}{R} = \frac{\mu_j^{\circ}}{RT_1} - \ln\left(\frac{N_j}{\sum_j N_j}\right) - \ln\left(\frac{P}{p^{\circ}}\right) \qquad \text{(I-1)}$$

where j ranges over the A representative molecular species. The N_j are determined by a mass balance using the $\{N^{\alpha}\}$ constraints of the problem. Thus the first estimates are evolved from the simultaneous solution of A linear equations. A method of selecting the characteristic molecular species required is presented next.

A reliable procedure for determining components has been found to proceed as follows. One first assumes that all of the atoms of species α are in their stable elemental form at the estimated temperature. This permits the determination of the number of moles of the A species assumed to be present. Using this information, a set of element potentials $\{\lambda_o^\alpha\}$ are generated as predicted by equation I-1. This permits the evaluation of a molecular composition vector $\{p_i\}_o$ where:

$$\{p_i\}_o = \{p^+ \exp[\frac{\lambda_o^\beta \omega_i^\beta}{R} - \frac{\mu_i^+}{RT}]\} \qquad \text{(I-2)}$$

This vector includes, if desired, all combinations of the atoms in molecular form for which thermodynamic data is available. For each atomic specie α, there will be an ordering of prevalence of the molecular species containing α. One selects the most prevalent representative of each atomic species to compute the new values of $\{\lambda^\alpha\}$, by satisfying the mass balance among these A component molecular species. When a particular molecular species is the most prevalent for more than one atomic specie, the requisite number of components to specify the problem are arrived at by selecting this and the next most prevalent molecular specie from the ordering list of the atomic types involved. In effect, a crude iteration is performed upon the $\{\lambda^\alpha\}$ at constant temperature. To arrive at the estimates, it is necessary to solve only one set of A simultaneous equations. The effect of this estimation technique is to bring the

molecular species into approximately the proportions they would exhibit in equilibrium at the estimated temperature, although not exactly. For many reactions the most prevalent species are known from experience, and the first step may be omitted.

It is worthwhile to note that this estimation technique breaks down when the reactants occur in stoichiometric proportions. In such instances, mass balance cannot be satisfied among the A component molecular species except by assigning the coefficient zero to one or more of them. Such an assignment would introduce a logarithmic infinity into the problem. This may be avoided by assigning some arbitrarily small, but finite, value to these vanishing coefficients. For example, the coefficient $0.005N^{\alpha}$ might be assigned to the vanishing component of element α. In this way, the estimation method may be used for all mixture proportions.

Several numerical examples are now presented to illustrate the estimation technique. The first example is that of the nitrogen tetroxide-hydrazine system which has been selected as the sample iterative calculation. See Part V. The mixture ratio selected (1.2:1) is slightly fuel rich from stoichiometric (1.44:1). The estimated temperature is 2500° K. The possible products were limited to eight molecular species for simplicity in demonstration. These correspond to the species of mole fraction greater than

10^{-4} in the equilibrium solution. The atomic species constraints have been determined to be

$$N^H = 0.05673 \text{ gr. at./gr.}$$

$$N^N = 0.04022 \text{ gr. at./gr.}$$

$$N^O = 0.02371 \text{ gr. at./gr.}$$

for this problem. The stable forms are diatomic molecules. The corresponding estimates of $\{\lambda_o^\alpha\}$ at 2500° K and 150 psia are

$$\frac{\lambda_o^H}{R} = -9.12$$

$$\frac{\lambda_o^N}{R} = -13.03$$

$$\frac{\lambda_o^O}{R} = -14.22$$

From this, the sample molecular species vector may be generated from equation I-2. The result is

	H	H_2	OH	H_2O	N_2	NO	O_2	O
$(p_i/p+)_o$	.055	4.76	2.829	1010.0	3.40	.1556	2.04	.0207

The representative molecular species are H_2, H_2O, and N_2 for the atomic species H, O, and N respectively.

The second example is that of nitrogen tetroxide and hydrazine in stoichiometric proportions. The pressure and assumed temperature are as in the preceeding example. The estimate $\{\lambda_o^\alpha\}$ of the parameters is

$$\frac{\lambda_o^H}{R} = -9.13$$

$$\frac{\lambda_o^N}{R} = -13.02$$

$$\frac{\lambda_o^O}{R} = -14.21$$

The corresponding molecular species vector is

	H	H_2	HO	H_2O	N_2	NO	O_2	O
$(p_i/p^+)_o$	0.054	4.618	2.829	1097.0	3.456	0.23	2.117	0.030

The components at stoichiometric conditions are H_2, N_2, and H_2O respectively. The coefficient of H_2 for the succeeding estimate is presumably zero, but is taken to be some small value, e.g., 0.005 N^H, to avoid the singularity mentioned.

To illustrate the application of the estimate technique to other mixtures and temperatures, the case of a hydrocarbon-oxygen system is selected. The mixture of reactants C_6H_2 + $5.5O_2$ is assumed. The temperature is assumed to be 4500° K, and the pressure 150 psia. The elemental products estimate is made for the C, H_2, and O_2 forms, and gives

$$\frac{\lambda_o^C}{R} = -2.72$$

$$\frac{\lambda_o^H}{R} = -11.17$$

$$\frac{\lambda_o^O}{R} = -15.12$$

The corresponding composition vector calculated from these is, for 9 species,

	C	CO	CO_2	H	H_2	HO	H_2O	O_2	O
$\ln(p_i/p+)_o$	1.57	15.69	13.94	1.13	-.22	1.25	0.21	1.48	2.0

The representative species are quite clearly CO, OH, CO_2 for C, H, O respectively. The abbreviated chemical reaction is therefore, $C_6H_2 + 5.5O_2 \longrightarrow 2OH + 3CO + 3CO_2$. Several other examples were calculated and the results satisfactorily predicted the accepted predominant species.

The reason that this estimate technique is an effective one in describing the element potentials is apparent from an investigation of the describing function, equation 23

$$\frac{\lambda^{\beta} w_i^{\beta}}{R} = \frac{\mu_i^{+}}{RT} + \ln\left(\frac{P}{p+}\right) + \ln\left(\frac{N_i}{N}\right)$$

The first term on the right is, by definition, only a function of the estimated temperature for a given species; the second is a function of the prescribed pressure. The third term is a function of the estimated temperature, the pressure and the atomic species constraints, and is therefore, the most difficult to estimate. Selecting the most prevalent molecular specie representative of atomic specie guarantees that $\ln \frac{N_i}{N}$ will take on its smallest magnitude and any error will reflect only small changes in the potentials $\{\lambda^{\alpha}\}$. The corresponding molecular species vector will accurately predict the mixture proportions at the estimated temperature.